

STUDIES ON STRAIGHT RUN GASOLINE

by

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STUDIES ON STRAIGHT RUN GASOLINE

INTRODUCTION

Straight run gasoline, as differentiated from cracked gasoline, is the product resulting from the simple distillation of crude oil. Approximately fifty per cent of the total gasoline production is that of straight run gasoline. In the early stages of the petroleum industry, straight run gasoline only was used, but with the development of the higher compression motor in the automotive industry, the tendency has been more and more to use the cracked product, because of its higher anti-knock rating. The result has been that the demand for straight run gasoline has decreased to an alarming extent, with a consequent reduction in price.

In the course of study on the subject of gasoline, it was thought advisable to determine the effect of air on the cracking of straight run gasoline in the vapor phase, and to determine if the amount of unsaturated bodies in the straight run gasoline could be increased by this method.

The straight run gasoline used in this work was supplied, gratis, by the Derby Oil Company of Wichita, Kansas.

LITERATURE

An investigation of the literature was made to determine what work, if any, had been done on this problem.

The Societe Anonyme des Combustibles Industriels (1), in 1906, obtained a patent on a process for partially dehydrogenating hydrocarbons by oxidizing them with a current of air at temperatures dependent upon the material being treated. Condensation of the dehydrogenated product then took place.

In the same year, the Societe Anonyme des Combustibles Industriels (2), obtained a patent for a method of distilling and partially dehydrogenating hydrocarbons. It consisted of heating them to a suitable temperature and, thereafter, without applying fire heat, blowing cold air through the mass, or cold air enriched with oxygen or an equivalent oxidizing agent. The air could also be mixed with inert gases such as carbon dioxide, nitrogen, or poor gases. Dehydrogenation of the hydrocarbons then took place by the exothermic oxidation reaction which also supplied enough heat to complete the distillation without additional fire heat.

A method was developed by Ramage (3), in 1917, for transforming hydrocarbons into compounds relatively poorer

in hydrogen by bringing their vapors into contact with a reducible metal oxide under such conditions as to effect a partial oxidation of the hydrogen of the hydrocarbon. The apparatus, for effecting this reaction, was comprised of heated tubes containing oxide, into which the hydrocarbon was delivered under pressure through a nozzle. By this process, it was claimed paraffins might be converted into olefins, as pentane into amylene.

In the following year, Ramage (4) converted high boiling hydrocarbons into low boiling hydrocarbons of the olefin series by passing oil vapors through heated tubes containing ferric oxide. The temperatures used to produce olefins were 600-680° Centigrade. The yields obtained were as high as ninety per cent. It was also found, that at higher temperatures and by the use of longer tubes, the olefins could be converted into aromatics.

Mardles (5), in 1928, in working with hexane-air mixtures, passed the vapors through a heated tube at various temperatures. The products of the reaction were collected and analysed.

The temperature of the furnace was varied from about 150° to 700° Centigrade. The products of the initial reaction were accompanied by a fine and very persistent fog, which passed through all the reagents without absorpt-

ion. The products isolated were aldehydes and acids. It was concluded that these were final products of decomposition of some more active and unstable compounds. The presence of active oxygen led to the belief that the initial products were organic peroxides.

The hot gases from the furnace were passed directly into slightly acidified potassium iodide solution and the liberated iodine was titrated with one-fiftieth normal sodium thiosulphate solution. There was only a very small quantity of active oxygen present when the gas mixture passing through the tube was heated longer than one minute, especially at high temperatures. With decreasing time of heating, much larger yields were obtained, especially when the mixture was not completely vaporized but was introduced in the form of a fine spray containing minute drops of liquid.

In a further attempt to isolate the peroxides, a condenser made of German silver, through which cold water circulated, was inserted into the exit end of the tube which was heated in a vertical position.

The condensate, when concentrated in a vacuum, left a gummy residue which did not detonate on heating. It consisted of decomposition products. It was concluded that the life of the primary peroxides was exceedingly

short on account of their thermal instability and reactivity.

In 1927, Lewis (6) enclosed a known quantity of liquid hydrocarbon and oxygen in a large cylindrical bulb and determined the pressure-temperature curve. The oxygen was substituted with air in some cases. He stated that whatever chemical change took place at the critical ignition temperature, the velocity was much greater with oxygen. The actual temperature of ignition, however, differed very little from that in determinations with air.

The contents of the bulb, after heating, were analyzed by qualitative tests. After cooling, the contents of the bulbs possessed a peculiar penetrating odor, resembling that of a terpene. Water, aldehydes, acids, and oxides of carbon were detected, but no peroxides. It was found, however, that a certain amount of gum was formed in the case of all paraffins. It was light yellow for moderate temperatures and black for high temperatures of formation. After investigating the formation of these gums it was assumed that they were condensation products of the aldehydes which were produced at the higher temperatures.

In 1928, a German firm, I. G. Farbenindustrie A.G. (7), obtained a patent for a process by which gaseous hydrocarbons, particularly saturated hydrocarbons such as

methane, were subjected to incomplete combustion with pure oxygen or a gas containing at least fifty per cent oxygen. Temperatures above 850° Centigrade were used to obtain unsaturated hydrocarbons, such as acetylene. The yield was found to increase when the products were heated to about 1200° Centigrade in an electric furnace.

Lewis (8), in 1929, strengthened the case for primary dehydrogenation by showing the comparison of the action of sulphur and of oxygen in the removal of hydrogen from saturated hydrocarbons. In his experiments, hexane vapor was drawn through molten sulphur at about 350° Centigrade by a current of nitrogen and a high yield of hydrogen sulphide resulted. The unattacked hexane recovered was found to contain one to two per cent by volume of unsaturated hydrocarbons.

Pope, Dykstra and Edgar (9), in 1929, passed mixtures of octane vapor and air through a heated glass tube and analyzed samples of the gas.

The method consisted of preheating and vaporizing the fuel in an atmosphere of nitrogen and mixing it, as suddenly as possible, with the requisite amount of oxygen when the desired furnace temperature had been reached. The final mixture of the gases contained about twenty and five-tenths per cent oxygen.

The gaseous oxidation products were carbon monoxide, carbon dioxide and a small amount of some gas absorbed by fuming sulphuric acid, the nature of which was not determined.

In 1929, Pease (10), in working with propane and butane, passed known volumes of hydrocarbon and air at known rates into a reaction tube and collected the gas which came off. The analysis of the gases was carried out with a Williams apparatus to which had been added a copper oxide combustion tube. In most of the experiments the furnace temperatures used were far below those required to produce appreciable dissociation.

The results of his experiments showed that unsaturated hydrocarbons were formed at temperatures of 500-600° Centigrade. Aldehydes were formed at temperatures of 300-350° Centigrade. The aldehyde reaction was found to be sensitive to relatively minor variations in the conditions of the reaction. Dilution with oxygen, methane, nitrogen, carbon dioxide and hydrogen depressed the reaction, increasingly, in the order named and the effect was greatest at higher temperatures.

From the results of his experiments, Pease states, "There is no essential physico-chemical difference between the reactions of the butanes with oxygen and those of

propane and that the same considerations are applicable. This being the case we are inclined to believe that the same will be true of the higher hydrocarbons."

Burwell (11), in 1929, treated normal liquid hydrocarbon material containing aliphatic compounds, such as a spindle oil petroleum distillate, in the liquid phase, with an oxidizing gas, such as air, at a temperature of at least 100° Centigrade. The process resulted in the formation of simple and hydroxy organic acids. An United States patent, 1,690,769, specifies contacting air with a normally liquid petroleum hydrocarbon mixture, such as forty-two degree Baume distillate from Pennsylvania petroleum. The conditions of temperature and pressure are the same. The products of the oxidation included water insoluble organic acids of solid or semi-solid character. These acids were also insoluble in the hydrocarbon mixture.

P. Mondain-Monval and B. Quenquin (12), in 1930, found that when pentane was mixed with air and heated to 325° Centigrade, fumes appeared and there was an increase in temperature of about 40°. The reaction took place with other compounds as follows: hexane at 530°, heptane at 325°, octane at 269°, and gasoline at 530° Centigrade. It was observed that, at the moment when the increase in

temperature was evident, a bluish luminescence appeared. If the gases were heated to the temperature used, prior to mixing, there was a delay of three seconds before oxidation occurred. At higher pressures the oxidation took place at lower temperatures but the delay was about thirty-five minutes.

Lewis (13), in 1930, determined the temperatures at which rapid oxidation set in during the slow heating of mixtures of hydrocarbons and oxygen in glass bulbs.

The results of his experiments were as follows:

Hydrocarbon	Minimum Ignition Temperature (Centigrade)
n-Pentane	255-257°
n-Hexane	232-233°
n-Heptane	218-220°
iso-Decane	210°

Brunner (14), in 1930, studied the slow oxidation, at 200-210° Centigrade, of a gas mixture containing forty-two per cent hexane in oxygen with three-tenths and one per cent respectively of aniline. By analysis of the gas mixture at various stages it was found that there was an initial induction period during which no reaction could be detected, followed by the true reaction forming water, peroxides, aldehydes, acids, carbon monoxide and carbon dioxide. The aniline which acted as a negative catalyst

was oxidized at the end of the induction period. The true oxidation was stated to take place in stages: Oxygen first being added to hydrogen in the molecule with the formation of unstable moloxides, which would break down to give water and an unsaturated compound which would add oxygen forming a peroxide.

Young (15), in 1930, obtained a patent for a process whereby a relatively cool mixture of oxygen and a hydrocarbon material, such as methane or a petroleum fraction, was passed into a reaction zone where a reacting temperature between 200 and 600° Centigrade was obtained. It was stated that the products of the reaction were comprised of alcohols and other derivatives.

P. Mondain-Monval and B. Quanquin (16), in 1931, formed from pentane, hexane, octane, and gasoline, by oxidation with air at about 300° Centigrade, an oily yellow mixture of peroxides. By operating a few degrees below the temperature at which white fumes appear, they obtained twenty to twenty-five cubic centimeters from seventy grams of hexane. The mixture was vacuum distilled. At 200° Centigrade it decomposed exothermally with a blue luminescence, but without flame, to give formaldehyde, other aldehydes and white fumes. When added to sodium hydroxide solution it evolved hydrogen, methyl alcohol and formic

acid. It was thought that acetic acid and probably its homologs were present.

James (17), in 1932, treated a finely divided hydrocarbon material, such as gas oil from Pennsylvania petroleum which is liquid at normal temperatures and pressures, with an oxygen containing gas, such as air. A stream of the mixture was passed through a hot reaction zone at a temperature below that of continuous self sustained complete combustion. The conditions were adjusted to produce a material percentage of alcohols.

Shimose (18), in 1931, obtained maleic acid as a main product, together with formaldehyde and carbon dioxide, through the catalytic oxidation of n-pentane, n-heptane, n-octane, 2-amylene and gasoline with air in the vapor phase.

Koravatzkii (19), in 1932, passed a mixture of a natural gas containing one to five per cent air, one-tenth per cent carbon dioxide, fifty-two to fifty-six per cent methane, ten to twelve per cent ethane, seventeen to twenty per cent propane and ten to twelve per cent higher hydrocarbons, and air through a furnace at definite temperatures. The gases were passed through a second furnace after the addition of more air. It was found that nitrogen tetroxide had a scarcely noticeable

catalytic effect and a copper catalyst caused much decomposition.

A yield, up to thirty-two per cent, of new liquid products was obtained from the oxidation. These products included alcohols, aldehydes and acids. The yields depended upon the concentration of oxygen and the velocity of the reaction. The best temperature was found to be 400-500° Centigrade. Temperatures of 600-700° Centigrade caused oxidation to carbon monoxide, unsaturated compounds, carbon dioxide and water. The condensate obtained, after the oxidation, contained up to ten per cent of formaldehyde, or two to three per cent of the charge.

Wiezevich and Tannich (20), in 1932, passed a mixture of low boiling aliphatic hydrocarbons, such as pentane, and air through a non-catalytic partial oxidation zone. This zone was under 300-3000 pounds per square inch pressure and temperatures of 200-600° Centigrade. Aliphatic acids were formed. These were neutralized by lime and the salts separated out. The unreacted material was then recycled.

Schmidt, Treppenhauer, Grossknisky and Fisher (21), in 1932, formed olefins or di-olefins, by bringing cyclic paraffins or olefins in the vapor phase into contact with a mass of anthracite at a raised temperature. It was

stated that the reaction then would take place in the presence of a diluent or at reduced pressures. In an example, hexamethylene vapor and steam were led over a mass of anthracite in a porcelain contact furnace to produce a ninety per cent yield of olefins consisting principally of ethylene.

Suida (22), in 1932, heated brown coal tar, or oils derived therefrom, or mineral oils, or their distillation residues, with steam to temperatures of 700-800° Centigrade under an absolute pressure not exceeding one hundred millimeters of mercury. The reaction was effected in the absence of a catalyst. The amount of steam was one third to three times that of the oil. Gases rich in olefins were obtained.

The Standard Oil Development Company (23), in 1932, patented a process for the direct oxidation of hydrocarbons under pressure by means of oxygen or a gas containing oxygen. The hydrocarbons, subjected to a pressure of seven atmospheres in the liquid state, were mixed with oxygen and discharged rapidly into an oxidation zone at a temperature of 600° Centigrade. The products were collected and the oxygenated compounds separated. The products from liquid pentane, by this method, contained acetic acid, methanol, acetone, ethanol propanol and butanol.

James (24), in 1932, obtained partial oxidation products from material, such as hydrocarbons, by feeding the material in a finely divided condition into contact with a solid oxidant material, such as molybdenum oxide. This was capable of yielding oxygen to the organic material. The treated material was then withdrawn from the reaction zone and subjected to reoxidizing by recycling.

The oxidation of hydrocarbons by air in the cases cited in the literature has been, in many cases, carried farther than was desired in this problem. According to Story, Provine and Bennett (25) the successive oxidation products of the olefins are as follows: peroxide, aldehyde, ketone, oxide, acid, carbon dioxide and water. This conforms with the theory of Brunner (14), which has been stated before, in all details except the initial oxidation product which according to Brunner is a moloxide which breaks down into an unsaturated compound. It is evident that, the cases in which acids, carbon dioxide and water have been produced, that the oxidation has been carried practically to completion.

The partial oxidation of hydrocarbons has resulted in olefins, peroxides, aldehydes and ketones. These reactions have necessitated accurate means of control. Their respective yields have been subject to variations in

the conditions under which the reaction took place. This was found to be true especially in the case cited by Pease (10).

Out of the various factors which may influence the nature of the product, it has been shown that a relatively higher temperature is necessary for the formation of olefins. This does not necessarily mean that olefins are the only compounds formed but the predominant one.

Several cases have been cited in which the hydrocarbon material has been gasoline, or a petroleum fraction. The nature of the products from these materials and the methods of treatment have varied considerably.

EXPERIMENTAL

Introduction

Any process involves variables such as temperature, time, concentration, pressure and catalyst. The variables, in the course of this study, were limited to two, namely temperature and concentration. The pressure variable was eliminated by performing all the experiments at atmospheric pressure. The variable time was controlled by maintaining a constant rate of hydrocarbon input. No catalysts were used.

Procedure

The general method of procedure, in the preliminary experiments, was as follows: The gasoline vapors, which were derived by distillation, were mixed with air and passed through a silica tube, seven-eighths inches in diameter and 19 inches long, wound with resistance wire and heavily insulated with asbestos. The hot vapors from the furnace passed through an insulated iron pipe, one-half inch in diameter and thirty-six inches long, and then into a water condenser. The per cent of unsaturation of the condensate was then determined.

The procedure for the main experiments differed only in the method of vaporizing the gasoline, which consisted in dropping the gasoline into a flask immersed in an oil bath maintained at a constant temperature. Additional tests such as, acid, doctor, corrosion, gum, aldehyde and peroxide were also made.

Data

The experiments have been divided into three groups because of differences in procedure and materials used.

Table I

Number	Temperature (Centigrade)	Liters Air per 100 cc. gasoline	Per Cent Unsaturation
1	370	0.00	10.8
2	370	0.75	11.0
3	370	3.50	12.0
4	370	6.00	14.0
5	370	12.00	17.0

Note: The gasoline used contained ten per cent unsaturation and was vaporized by distillation.

Table II

Number	Temperature (Centigrade)	Liters Air per 100 cc. gasoline	Per Cent Unsaturation
1	370	12.0	21.0
2	640	0.0	13.3
3	640	7.0	33.0
4	640	10.0	37.5

Note: The gasoline used contained ten per cent unsaturation and was vaporized at a constant temperature.

Table III

Number	Temperature °C	Liters Air per 100 cc. gasoline	Per Cent Unsaturation.	Grams Gum per 100 cc. gasoline
1	255	0.0	2.0	.0202
2	255	7.0	2.1	.0324
3	255	13.5	3.0	.0428
4	320	0.0	2.4	.0216
5	320	1.5	4.0	.0300
6	320	8.0	7.8	.0800
7	320	11.5	11.0	.0980
8	360	0.0	2.7	.0284
9	360	5.1	7.0	.0676
10	360	9.5	9.4	.0720
11	360	11.0	10.0	.0832
12	360	13.5	12.0	.0916
13	400	0.0	3.4	.0182
14	400	1.4	5.0	.0184
15	400	6.5	8.75	.0460
16	400	8.0	11.0	.0476
17	400	12.5	12.0	.0850
18	640	0.0	5.0	.0208
19	640	1.9	8.0	.0464
20	640	4.5	9.3	.0680
21	640	6.5	10.7	.0820
22	640	14.8	17.0	.0844

Note: The gasoline used contained two per cent unsaturation and was vaporized at a constant temperature.

Notes

An attempt was made to preheat the air by passing it through a heated metal tube coil. It was found that the temperature of the air was dependent on the velocity through the preheater and, in order to obtain the desired temperatures, the velocity of the air had to be such that it prohibited condensation of the products.

The tests for unsaturation, gum corrosion, doctor and acid were performed according to the United States Government Specifications (26).

To determine aldehydes (27) Fuchsin Aldehyde Reagent was used. Two or three drops of the gasoline sample were added to five cubic centimeters of the reagent. After shaking, this was allowed to stand for two minutes. The appearance of a distinct pink, red, purple or blue color within the time limit is considered a positive test.

The test for peroxides was carried out with a reagent, described by Yule and Wilson (28), which consisted of, fifty grams of ferrous sulphate, fifty grams of ammonium thiocyanate, fifty cubic centimeters of sulphuric acid, five thousand cubic centimeters of water and five thousand cubic centimeters of acetone. About one cubic centimeter of the reagent is used in testing and the appearance

of a red color is indicative of peroxides.

A white uncondensable fog was formed in many of the runs. In order to prevent the loss of this material, the vapors were passed through a series of bottles containing mineral oil.

It was found, by passing these vapors into a tirrell burner and igniting, that they burned with a yellow luminous flame. By bringing the fog into contact with solid carbon dioxide, some of the material was solidified. When the solid carbon dioxide was almost exhausted, the vapors arising from the container were ignited and they burned with a yellow flame. It was also found, by passing these vapors through sulphuric acid, that most of them were absorbed. The acid became dark in color and a tar was formed.

All of the gasoline samples produced, in the runs of Table III, when air was used, were found to contain dissolved aldehydes. No aldehydes were found in the products of the runs in which no air was used until a temperature of 640° Centigrade was reached.

In runs 7, 11, 12, 18, 21 and 22 of Table III, an oily liquid was produced which, while insoluble in the condensate, was soluble in water. The color of the liquid varied from brown at low temperatures to dark red

at high temperatures of formation. It was found to give a strong positive test with Fuchsin Aldehyde Reagent.

The original gasoline was determined by test to be doctor sour but not acid to litmus. It was found that the runs of Table III produced a gasoline which was acid to litmus. In the runs in which no air was used the products were doctor sour. The products from the runs, in which air was used, were all found to be doctor sweet.

All of the samples were found to be negative toward the peroxide test except two, which were numbers 15 and 21.

Discussion

It is shown, by the results of the experiments, that for any one temperature, the per cent of unsaturation increased as the amount of air was increased. This was found to be the case in all of the runs. The oxygen of the air, apparently, has a major role in the conversion, although its effect is dependent on the temperature, which is shown by the fact that the increase in unsaturation is greatest at the higher temperatures.

The effect of temperature alone on the degree of unsaturation is shown by two different groups of runs, such as experiments numbers, 2, 6, 9, 15, 21 and 3, 7, 12 and 22, of Table III. In each of these groups, the volume of

air used was practically the same but the unsaturation increased with each succeeding higher temperature. Other examples are found in runs numbers, 12 and 17, and 7 and 16. The temperature effect is shown by the fact that a low concentration of air at a high temperature produced approximately the same degree of unsaturation as a high concentration of air at a low temperature.

In the experiments, where no air was used, the unsaturation increased as the temperature increased. This is evidently due to some cracking on vaporization, which was indicated by the appearance of a small quantity of white fumes in the flask, and thermal decomposition in the reaction zone. These runs also show that the total increase in unsaturation, in the runs in which air was used, is almost entirely due to the action of the air rather than the temperature.

The effect of cracking and decomposition is also shown by runs numbers 1 of Table II and 5 of Table I, in which the same conditions of temperature and air concentration prevailed but the resulting degree of unsaturation differed.

The conversion of the raw material, which was neutral and doctor sour, into a gasoline which was doctor sweet and acid to litmus may be due to the oxidation of the

sulphur, in the sulphur compounds, which causes a sour doctor test, into sulphur dioxide. The acidity of the products then could be due to the absorption of the sulphur dioxide.

The aldehydes that were formed are probably the result of the oxidation of some of the original unsaturated compounds and the unsaturated compounds formed in the reaction zone. These were formed only in small quantities and the value of the gasoline as a motor fuel would not be influenced since they are readily removed by the sodium hydroxide wash.

The volume of the fog produced was found to be the greatest at high temperatures. The effect of the air on the production of the fog was shown by the fact that at a constant temperature the volume of fog increased with an increasing volume of air. Fog was not produced in the runs without air until a temperature of 640° Centigrade was reached where only a small amount was observed.

It may be stated that the products contained in the fog, as a result of their reaction with sulphuric acid, might reasonably be olefins, for according to Trusty (29) "The group of hydrocarbons most affected by acid treatment are the olefins or unsaturated compounds. Sulphuric acid absorbs some of the olefins and polymerizes others.

Leslie (Motor Fuels) states that the mono-olefins are not polymerized to tars, but that these tars formed during acid treatment are caused by polymerization of di-olefins."

The method of vaporization, which was carried out at constant temperature, had many advantages over that of distillation. In distillation, as the composition varied the temperature also varied and the lighter fractions of the gasoline had a lower temperature than the heavier fractions at the initial contact with the air and a longer period of contact with the walls of the furnace was necessary to attain the maximum temperature. By the constant temperature method, the gasoline was instantly vaporized on contact with the flask, since the temperature of the flask was higher than the highest boiling component of the gasoline, and the vapors then entered the furnace at a constant temperature and composition.

The gum content of the gasoline was found to increase as the unsaturation of the product increased. This gives some insight as to the nature of the unsaturation.

According to Brooks (30), the first step in the formation of gum in cracked gasolines is the formation of organic peroxides. These break up in a complex manner, with the formation of aldehydes, ketones, water, carbon dioxide and further oxidation to organic acids.

This is confirmed by Story, Provine and Bennett (25) who state that the organic peroxides are apparently a result of the oxidation of unsaturated hydrocarbons. The decomposition of the peroxides then takes place in the manner stated by Brooks (30). It was also stated that physical characteristics and composition of the acids, which are the end products, point toward polymers of unsaturated acids. The original hydrocarbons then may have been compounds containing conjugated double bonds.

The gum formed, in the samples analyzed, is not likely to be due to the peroxides, aldehydes or acids formed in the reaction, since the gasoline sample was washed with both sodium hydroxide solution and water before an analysis was made. This treatment would neutralize the acids and according to Yule and Wilson (28), the caustic soda immediately removes a small amount of the peroxides and the remainder is gradually removed by continued shaking. The aldehydes are also removed by this treatment. It was found that a gasoline which was positive toward Fuchsin Aldehyde Reagent before the wash was negative afterwards.

Therefore the gum found in the samples is probably due to di-olefins which oxidize on evaporation, according to the method stated by Brooks (30).

Any increase in the olefin content of the straight run

gasoline would make it more desirable for a motor fuel for it has been found that the anti-knock properties of the hydrocarbons in gasoline increase in the following order: paraffin, unsaturated, naphthene and aromatic hydrocarbons. According to Bowen (31), "Each olefin exerts a different influence as a knock suppressor and this in turn is dependent upon its chemical composition or structure. Liquid olefins with more than one double linkage probably have very good knock ratings but must be removed when their gumming tendencies are too pronounced." The gum content of the samples has not been excessive and it, probably, could be lowered by acid treatment without impairing the degree of unsaturation to a great extent.

Many reactions of oxygen with hydrocarbons are thermodynamically possible and the reactions under different conditions of oxygen concentration and experimental technique may follow different courses.

Lewis (8) has pointed out that the ease with which hydrogen is removed from saturated hydrocarbons varies with the structure and that unsaturated hydrocarbons can be obtained from the paraffins by partial oxidation under special conditions.

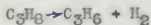
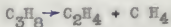
Beall (32) states that, in the oxidation of a saturated hydrocarbon, hydrogen combines with the oxygen and

is removed as water. Another portion of the oxygen may combine to form compounds of carbon, hydrogen and oxygen and also the oxides of carbon. The oxidation of a saturated hydrocarbon to produce an unsaturated hydrocarbon may be represented thus:



All of these oxidation reactions are exothermic and a temperature rise results because of the internal release of heat. This internal release of heat affords a rapid means of heat exchange with the unreacted components of the system. It is evident that if there is sufficient oxidation the temperatures will rise to where cracking of some of the original hydrocarbons will result. This system then has an advantage over straight cracking in that there are possibilities of synthesis, rearrangement and decomposition.

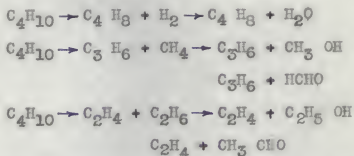
When the heat liberated from the oxidation reaction is sufficient for thermal dissociation of the hydrocarbons, the reaction, as stated by Pease (10), may be represented as:



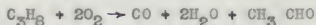
Thermal dissociation would only account for a portion of the unsaturated hydrocarbons formed. The remainder

then must be a product of oxidation. According to Pease (l.c.), the reactions cannot be definitely stated but they may be regarded as oxidations of those portions of the molecules which would be split off in dissociation leaving olefins.

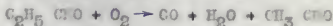
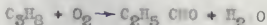
For example:



Another type of reaction which may occur in the oxidation of hydrocarbons is the aldehyde reaction. It was found by Pease (l.c.) that this reaction takes place at lower temperatures than that required for the reaction to produce unsaturated hydrocarbons. This aldehyde reaction is subject to suppression by diluents such as oxygen, methane, nitrogen, carbon dioxide, hydrogen and potassium chloride coating of the reaction chamber. Even under suppression and high temperatures, the reaction to produce olefins is accompanied by the production of aldehydes in varying amounts. Pease (l.c.), has represented the aldehyde reaction as:



Pease (l.c.) states that "This appears to be indicative of the type of reaction which Edgar and Pope (Swampscott Meeting 1928) have found in the case of the higher hydrocarbons and an example of which is:"



This conforms with later work of Pope, Dykstra and Edgar (9), in which they have found that the primary oxidation product of octane is an aldehyde and that this aldehyde is further oxidized with the formation of other aldehydes of lower molecular weight.

Brunner and Rideal (33), in working with n-hexane, have stated that "It seems probable that during the period of slow reaction, a number of chemical reactions involving peroxide molecules are taking place and the identification of small quantities of products isolated affords some slight experimental evidence for the following:

(1) Decomposition to the aldehyde and water, followed by partial further oxidation and condensation of the aldehyde produced.

(2) Reactions with hexane to produce unsaturated hydrocarbons and water. The unsaturated hydrocarbon produced under-going polymerization or further oxidation.

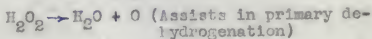
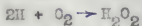
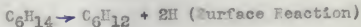
Lewis (6), in some of his earlier work, states that

"Two theories have been advanced to explain the primary action of oxidation of paraffin hydrocarbons: the older hydroxyl theory of ~~Wass~~ and the peroxide theory of Callendar. The latter theory possesses no advantage over the former and differs from it merely in postulating the interposition of two oxygen atoms in place of one between a C-H or C-C linkage. It is true that peroxides have been detected by passing vapor-air mixtures through heated tubes and suddenly cooling the products, the effective yield being increased when the experiment was carried out with droplets, but the experiments of Callendar are inconclusive in that they do not show definitely that the peroxides are alanyl or di-alkyl peroxides and not hydrogen peroxide. Even if the former are present they may be the result of secondary oxidations of unsaturated hydrocarbons previously produced, for these substances have been proved to yield peroxides readily."

As a result of experimental work, Lewis (6) has advanced a primary dehydrogenation theory in which he states that the primary oxidation consists in the direct combination of oxygen with those atoms of hydrogen which are most easily split off from the hydrocarbon molecule. The initial products being unsaturated hydrocarbons containing one or more double bonds and water. Secondary reactions then may occur in which the oxygen

combines with the unsaturated hydrocarbon to produce aldehydes and peroxides.

The primary oxidation reaction as represented by Lewis (8) is as follows:



This reaction under the conditions of temperature and pressure of the experiment was found to have a very low velocity except at the surface of the containing vessel.

CONCLUSIONS

1. The per cent of unsaturation of the finished product increased with increasing amounts of air, the temperature being maintained constant.
2. The per cent of unsaturation of the finished product increased with increasing temperature, the volume of air being maintained constant.
3. The gum content of the finished product increased with increasing amount of unsaturation.

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